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(54) ELECTRODE FOR LIQUID CRYSTAL DISPLAY

(57) Abstract:

PURPOSE: To simplify the production process and to obtain a stabilized forming condition favorable to production by forming a transparent conductive film with a ZnO film added with Ga.

CONSTITUTION: A plastic substrate having an electrode consisting of a transparent conductive film is used for an electrode liq. display, and a ZnO film incorporated with Ga is used as the transparent conductive film. The content of Ga is controlled to 0.5-20 atomic % of Ga plus Zn. The transparent conductive film is formed by sputtering with a ZnO sintered compact incorporated with Ga as a target. A large-area film is formed and a higher film forming rate of ≧7nmsec is realized by DC sputtering, and higher productivity is expected. Consequently, the adhesion between the substrate and film is enhanced, the patterning property is improved, and the plastic material to be used for the substrate is not restricted.

- ZnO + Ga

- f./a

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] This invention relates to the electrode for liquid crystal displays.
[0002]
[Description of the Prior Art] Although widely used as small indicators, such as instruments, from before, promising ** is most carried out recently, development of an electrochromatic display display device progressing by the advance of a detailed-ized technique etc., and using a liquid crystal display component as the technique which enables lightweight-izing of the display screen which is the problem of the Braun tube, and sheet metal-ization. It is actually spreading through the image display of small television or a portable personal computer quickly. Although the approach of producing and panel-izing a liquid crystal display component on a glass substrate is now main, compared with the glass substrate, that workability is easy, lightweight being a thing, that deformation is possible, it being hard to be divided, and a plastic plate since it is cheap attract attention, and it is coming for the first time recently.
[0003] It is In 2O3 by which Sn was added on the other hand since it said conventionally that specific resistance was low as transparence electric conduction film for electrodes formed on the glass substrate of the electrode for liquid crystal displays. The film (ITO) is common. However, in using the ITO film for a plastic plate, some technical problems occur.
[0004] Since the ITO film needs to raise substrate temperature at the time of membrane formation in order to obtain high conductivity, only the plastic material which can bear this high substrate temperature can be used a membrane formation process not only becomes complicated, but, but the ingredient which can be adapted has a limit.
[0005] moreover -- although the transparence electric conduction film is etched in the case of electrode production by patterning, since the ITO film has high chemical stability -- as an etching agent -- FeCl2 etc. -- it is necessary to use the strong acid containing a reducing agent For this reason, the plastic plate which can bear such a strong etching agent must be used.
[0006] Since the crystallinity acquired with membrane formation temperature differs, an etch rate changes with membrane formation conditions, or dispersion comes out of the ITO film to an etch rate under the effect of the internal stress of the comparatively large film generated after membrane formation, and the sharpness of patterning is furthermore hard to be obtained.
[0007] And when the direct ITO film was formed in plastics, not only adhesion reinforcement with a substrate is low, but there was a problem of a plastic plate front face deteriorating by the plasma of oxygen gas required as a membrane formation ambient atmosphere.
[0008] In order to conquer these problems, the technique of performing special surface treatment to a plastic plate front face is examined. For example, the etching-proof agent nature of a plastic plate, a water resisting property, gas barrier property, and for the purpose of the improvement in adhesion with the ITO film, a metal oxide film is formed in a plastic plate front face, and forming the ITO film of the transparence electric conduction film for electrodes further after that is proposed (JP,54-12602,B). However, a film configuration becomes complicated and the problem that a production process also increases is expected.
[0009] By the way, if possible [since expensive In is a principal component, the ITO film has high ingredient

cost, and], conversion on other cheap transparence electric conduction film is desired. As transparence electric conduction film other than the ITO film, it is the ZnO film and SnO2. The film is known.
[0010] Although, as for the ZnO film, addition of aluminum, In, B, etc. is tried for the purpose of the reduction in resistance by low-temperature membrane formation since specific resistance is high, only about [1x10-3ohmcm] specific resistance is obtained. Then, the method of performing heat treatment in a vacuum is after membrane formation for the purpose of raising transparency and conductivity, and a production process becomes complicated and leads also to a cost rise. It is thought from the above reason that use is difficult for the ZnO film as transparence electric conduction film for electrodes of the electrode for liquid crystal displays.
[0011] Moreover, SnO2 Since it is necessary to use a CVD method with high substrate temperature in order for the film to obtain high conductivity, now, it is thought that application on the transparence electric conduction film for electrodes of the electrode for liquid crystal displays on a plastic plate is difficult.
[0012]
[Problem(s) to be Solved by the Invention] This invention aims at offer of the electrode for liquid crystal displays which does not receive constraint of the plastic material used for a substrate. Moreover, it aims at offer of the electrode for liquid crystal displays which was excellent in conductivity and patterning nature and was excellent also in processing cost and productivity. Furthermore, the adhesion of a substrate and the film is high and aims at offer of the electrode for liquid crystal displays which can be formed, without using the oxygen gas which degrades a substrate front face.
[0013]
[Means for Solving the Problem] In the electrode for liquid crystal displays using the plastic plate which has the electrode with which this invention consists of transparence electric conduction film, the electrode for liquid crystal displays characterized by this transparence electric conduction film being ZnO film with which Ga was added is offered.
[0014] Since room temperature membrane formation is also crystalline good high transparence electric conduction film, the ZnO (henceforth GZO) film with which Ga used by this invention was added has the unnecessary vacuum heat treatment of the film after the membrane formation for discovering required high permeability and low resistance by the conventional ZnO film. Therefore, while production equipment can be simplified, the damage to the plastic plate by heating is avoidable. Therefore, as an ingredient of a plastic plate, general-purpose plastic material, such as polyester, polyether sulphone, a polycarbonate, acrylic resin, and polyarylate, can be used.
[0015] in order to raise the adhesion of the GZO film and a plastic plate -- SiO2 etc. -- although inorganic surface treatment can also be performed, since the GZO film in this invention can be formed in an argon ambient atmosphere, it does not have degradation by the oxygen gas plasma, and can also be directly formed on a plastic plate.
[0016] Since the GZO film formed on the plastic plate can be easily etched with the weak acid liquid of ordinary temperature, it excels in patterning nature and the plastics of a substrate is not degraded at the process of patterning.
[0017] Below 20 atom % of the content rate of Ga in the GZO film is desirable more than 0.5 atom % to total of the metal atom of the point of the internal stress of conductivity or the film to Ga and Zn.
[0018] Although it can be manufactured with a RF-sputtering method, the DC sputtering method, a vacuum deposition method, a chemical-vapor-deposition method, and the other membrane formation techniques of arbitration, its adhesion to a substrate is high, and since the creation approach of the GZO film tends to control Ga addition, forming using the sputtering method is desirable [the approach].
[0019] the case of the sputtering method -- as the target of a raw material -- a metal and an oxide -- although both can be formed, in order to fully demonstrate the function offered by this invention, it is most desirable to use as a target the sintered compact of ZnO with which Ga was added.
[0020] Since the sintered compact of GZO has conductivity, by the DC sputtering method comparatively cheap as a production machine, large area membrane formation and a high 7nm [/second] or more membrane formation rate can be realized, and improvement in productivity can be expected.
[0021]
[Function] Since the GZO film can be formed in the ambient atmosphere of only inert gas while it can carry out

[low ****]-izing also in low-temperature membrane formation more than the ITO film and an EQC, since reactant gas like oxygen gas does not exist, there is no problem of control of a reaction, and film formation by which various properties were stabilized can be performed.
[0022] For this reason, formation of the transparence electric conduction film is attained with substrate heating at the time of membrane formation, and the plasma-ized reactant gas, without degrading various properties, such as permeability of a plastic plate.
[0023] Moreover, at the etching process in the case of patterning, since a weak acid solution can be used for the GZO film in this invention as an etching solution, it can carry out patterning of the electrode, without making a plastic plate corrode. When the GZO film of this invention is used as the transparence electric conduction film for electrodes from these reasons, the range of the ingredient of the plastic plate which can be adapted can be extended.
[0024] Furthermore, since cheap membrane formation equipment can be used and a membrane formation rate becomes quick when the DC sputtering method is used as the membrane formation approach, a cost cut is possible. Moreover, since the ZnO system is cheap as compared with expensive ITO, the cost cut of the cost of materials can also do a raw material.
[0025]
[Example]
By [example 1 and examples 1-2 of comparison] 30cmx26cm, about 300nm various transparence electric conduction film was formed by the DC sputtering method on the polycarbonate resin substrate with a thickness of 0.4mm about the case where substrate temperature is 25 degrees C and 100 degrees C. The presentation of the transparence electric conduction film with which it was obtained in any case was almost the same as the presentation of the used target. In addition, since film exfoliation arose in the example 1 of a comparison when membranes were directly formed on the substrate, it is SiO2 as substrate film. The film was formed.
[0026] The membrane formation conditions at this time, and the obtained membranous specific resistance and the membranous membrane formation rate are shown in Table 1. The maximum power flux density and the maximum membrane formation rate which can be supplied were also measured, and it was shown in Table 1. The addition rate of the addition metal in the target shown in front Naka is an amount to total of all the metal atoms in a target. Moreover, O2 in the sputtering ambient atmosphere in the example 1 of a comparison An amount is Ar and O2. It is one volume % to total.
[0027] In the example 2, the [example 3 of comparison] example 1, and the example 1 of a comparison, about the GZO film and ITO film which were formed at the substrate temperature of 100 degrees C, the photolithography method was used on each of that transparence electric conduction film, the pattern was produced, it etched with the monograph affair shown in Table 2, the resist was removed after that, and the damage of the etch rate of each transparence electric conduction film, patterning nature, and a substrate was investigated. A result is shown in Table 2.
[0028] By [examples 3-4 and examples 4-5 of comparison] 30cmx26cm, the GZO film, the ITO film, and the aluminum addition ZnO (henceforth AZO) film were formed by the DC sputtering method on the polycarbonate resin substrate with a thickness of 0.4mm at about 300nm of thickness, respectively. In addition, the presentation of the used target is the same as the case of Table 1 respectively. Substrate temperature was made [film / GZO] into 100 degrees C about a room temperature and 100 degrees C, the ITO film, and the AZO film.
[0029] Patterning was carried out to the predetermined electrode configuration with the weak acidic etching solution after membrane formation. The electrode for a TN liquid crystal display was produced with this polycarbonate resin substrate with an electrode.
[0030] Change of the capacity frequency characteristics in 1kHz before and behind a heat-resistant humidity resistance test and DC energization trial, i.e., specific-inductive-capacity epsilon'**, was measured in order to evaluate dependability about the obtained electrode for liquid crystal displays. Moreover, change of the alternating current value before and behind a heat-resistant humidity resistance test and DC energization trial (muA) was measured. The electrical potential differences of this alternating current are a sin wave, 32Hz, and 3 VP-P. In addition, heat-resistant humidity resistance test conditions are 80 degrees C, RH90%, and 500 hours, and DC energization test condition is 5 V or 500 hours. These results are shown in Table 3.

[0031] As shown in Table 3, also in low-temperature membrane formation of 100 degrees C or less, the electrode for liquid crystal displays of this invention using the GZO film has small capacity frequency characteristics and rate of an alternating current value change before and behind a heat-resistant humidity resistance test and DC energization trial, and is excellent in dependability.

[0032]

[Table 1]

	実施例１	比較例１	比較例２
ターゲット	５原子％Ｇａ添加のＺｎＯ	７．５原子％Ｓｎ添加のＩＴＯ	２．５原子％Ａｌ添加のＺｎＯ
雰囲気	Ａｒ	Ａｒ＋O_2	Ａｒ
比抵抗（Ωｃｍ）			
（成膜温度２５℃）	4×10^{-4}	7×10^{-4}	2×10^{-3}
（成膜温度１００℃）	3×10^{-4}	5×10^{-4}	1×10^{-3}
単位電力密度W/cm^2 あたりの成膜速度（nm/s）	１．３	１．３	１．０
最大電力密度（W/cm^2）	７．０	４．０	２．０
最大成膜速度（nm/s）	９．１	５．２	２．０

[0033]

[Table 2]

	実施例２	比較例３
透明導電膜	ＧＺＯ	ＩＴＯ
エッチング剤 エッチング条件	0.1N HCl水溶液 室温、３０秒、撹拌なし	$FeCl_3$ ＋HCl 水溶液 室温、１分、撹拌なし
エッチング速度	０．６μｍ／分	０．３μｍ／分
パターニング性 シャープネス オーバーエッチング 再現性	◎ 良好 なし 歪み位置ずれなし	△ エッチング面凹凸あり 少々あり 端部に歪み位置ずれあり
基板のダメージ	なし	なし

[0034]

[Table 3]

		実施例３	実施例４	比較例４	比較例５
		ＧＺＯ膜	ＧＺＯ膜	ＩＴＯ膜	ＡＺＯ膜
		室温	100℃	100℃	100℃
比誘電率ε′					
耐熱耐湿	初期	6.5	7.4	8.4	9.0
	500時間	7.0	7.8	12.5	19.2
	変化率	1.08	1.05	1.49	2.13
ＤＣ通電	初期	7.3	6.7	6.0	8.9
	500時間	7.3	6.7	6.0	15.6
	変化率	1.0	1.0	1.0	1.7
交流電流値（μＡ）					
耐熱耐湿	初期	0.46	0.46	0.48	0.50
	500時間	0.79	0.85	7.10	17.3
	変化率	1.72	1.85	14.79	34.6
ＤＣ通電	初期	0.50	0.50	0.60	0.50
	500時間	0.49	0.50	0.58	1.4
	変化率	0.99	1.0	0.97	2.8

[0035]
[Effect of the Invention] In the process of manufacture, as for the electrode for liquid crystal displays of this invention, oxygen gas has high conductivity unnecessarily [substrate heating] unnecessarily. Therefore, a manufacture process can be simplified and the desirable stable formation conditions are acquired by production.

[0036] Moreover, the electrode for liquid crystal displays of this invention does not have constraint of the plastic material used for a substrate, either, while the adhesion of a substrate and the film is high and patterning nature is excellent.
[0037] Moreover, if the sputtering method is used, since conductivity is in a target, membrane formation to the large area substrate by DC sputtering can be performed.
[0038] Since the formation rate is fully large even if it compares with the further existing transparence electric conduction film, productivity can be raised sharply.
[0039] Moreover, since it is cheap compared with the conventional ITO film, raw material expense combines with high-speed membrane formation, and the creation of the cheap electrode for liquid crystal displays of it is attained.

[Translation done.]